

## OBTAINING OF COUMARONE-INDENE RESINS BASED ON LIGHT FRACTION OF COAL TAR

### 1. COUMARONE-INDENE RESINS WITH CARBOXY GROUPS

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**Abstract.** Coumarone-indene resins (CIR) with carboxy groups were synthesized *via* cooligomerization of unsaturated compounds presented in light fraction of coal tar and its fraction boiling out within 423–463 K with the addition of such industrial monomers as styrene, maleic anhydride, glycidyl methacrylate and methacrylic acid. 2,2'-Azobis(2-methylpropionitrile) in the form of 0.2 M solution in toluene was used as an initiator. The effect of monomers nature, initiator amount, temperature and reaction time on the yield and characteristics of resulted CIR has been determined. The structure of the synthesized CIR was confirmed by IR-spectroscopy. The conversion of unsaturated compounds during synthesis of CIR with carboxy groups was determined by gas-liquid chromatography.

**Keywords:** light fraction of coal tar, coumarone-indene resin, styrene, maleic anhydride, glycidyl methacrylate, methacrylic acid, 2,2'-azobis(2-methylpropionitrile), cooligomerization, IR-spectroscopy, gas-liquid chromatography.

## 1. Introduction

Coal tar is a by-product of the coking process [1]. After coal tar rectification the so called light fraction of coal tar (LFCT) is produced. This light fraction contains high-boiling unsaturated compounds, in particular indene, coumarone, styrene, and other hydrocarbons [2].

One of the ways of LFCT rational usage is obtaining of coumarone-indene resins (CIR) on its basis [2-7]. CIR may be obtained according to radical [2, 6] or ionic [2, 7] mechanisms. If radical mechanism takes place, CIR are produced due to the thermal cooligomerization of

unsaturated compounds present in the initial fraction [2] or by using initiators [6]. If cooligomerization of unsaturated compounds takes place *via* ionic mechanism, then acid catalysis occurs [2, 7]. More prevalent in industry is the production method *via* ionic mechanism using Lewis acid, Brønsted acid and their mixtures as the catalysts. CIR of various colors with different softening temperatures are obtained. The quality and the amount of the products depend on synthesis conditions, catalyst nature and characteristics of the raw materials [2].

According to the modern theory of carb-cation reactions mechanism at least one double bond must remain in the CIR cooligomerization products. The products ability to add bromine or iodine confirms this fact. Cooligomerization products may consist of the same (oligomers or polymers) or different chains (copolymers or cooligomers). In most references they are given as unbranched structures (Fig. 1).

The cooligomers structure may also have a nonlinear form. The simplest example is diindene (Fig. 2).

The compounds with several unsaturated bonds may be formed as well, for instance as a result of carb-cation addition to already formed macromolecule or participation of dienic hydrocarbons in the reaction. Two possible structures are represented in Fig. 3. The unsaturation of the obtained resins is higher in the latter case.

Thermal polymerization resins compared with those obtained *via* catalytic cooligomerization have better properties to be used in paint-and-varnish industry. However, this process needs high temperatures (438–523 K), pressure (0.6 MPa) and reaction time of 3–72 h [2]. Initiated cooligomerization of unsaturated compounds contained in the initial indene-coumarone fraction has been studied less. The initiation, *i.e.* radicals obtaining, is carried out due to physico-chemical influence on the raw material, in particular photoinitiation, electroinitiation, *etc.* Very often the process is combined with CIR modification by acids, ethers, esters and other unsaturated compounds [2, 7]. The resulted resins are actually insoluble in organic solvents and have high melting temperatures.

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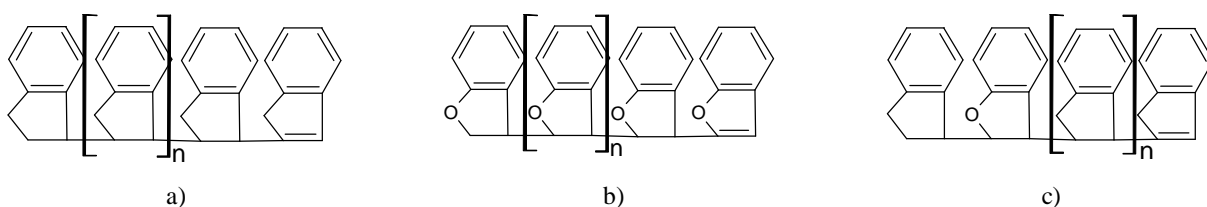
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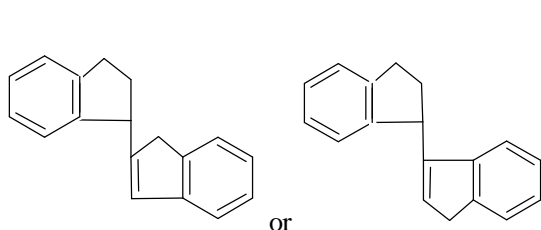
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During last years the researches of the Department of Petroleum Chemistry and Technology (Lviv Polytechnic National University, Lviv, Ukraine) carried out investigations concerning CIR obtaining and its using as polymeric components for polymers modified bitumen production [8]. To synthesize CIR we used cooligomerization of unsaturated compounds contained in the indene-coumarone fraction which was obtained from heavy gasoline fraction of by-product-coking production. The obtained CIR are used as additives for bitumen in the amount of 7–8 wt % relative to the resulted mixture [4, 5, 8].

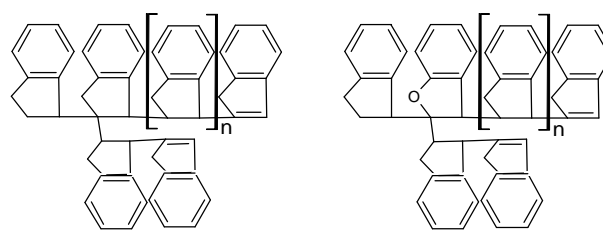
Taking all mentioned into account, the development of new methods of obtaining CIR and introducing various functional groups into their structure were found to be prospective. Moreover, to extend the source of raw material it would be interesting to obtain CIR based on a light fraction of coal tar. On the other hand, the introduction of different functional groups into CIR structure would allow to improve the operational properties of polymers modified bitumen with the simultaneous decrease of CIR content in it.



**Fig. 1.** Linear unbranched structures of CIR cooligomerization products: polyindene (a); polycoumarone (b); indene + coumarone copolymer (c)



**Fig. 2.** Diindene



**Fig. 3.** Branched structures of CIR cooligomerization products

*Table 1*

**Components content in raw materials**

Component	Component content, wt %	
	LFCT	ICF
Benzene	35.1	1.3
Toluene	23.8	10.3
Ethylbenzene	1.8	2.4
<i>m</i> + <i>p</i> -Xylenes	17.6	25.8
<i>o</i> -Xylene	2.3	4.3
Styrene	1.2	2.5
<i>n</i> -Ethyl toluene	–	2.7
<i>o</i> -Ethyl toluene	–	2.4
Pseudocumene	1.2	3.4
Hidrindane	4.4	12.8
Coumarone	1.3	3.5
Indene	3.9	11.1
Naphthalene	1.8	4.0
<i>b</i> -Methylnaphthalene	3.0	8.8
<i>a</i> -Methylnaphthalene	0.5	1.6
Other hydrocarbons	2.1	3.1
Total	100	100

## 2. Experimental

### 2.1. Materials

The raw materials for CIR synthesis were light fraction of coal tar (LFCT), produced at JSC "Zaporizhkoks" (Ukraine), and indene-coumarone fraction with the boiling range of 423–463 K (ICF) which was distilled off LFCT. The components content is represented in Table 1.

Following modifiers were used for cooligomerization of unsaturated compounds:

- styrene, which was dried before the experiments with solid alkali and purified by distillation at 323 K under residue pressure of 300–400 Pa. Its characteristics: refractive index  $n_D^{20} = 1.5471$  (literature value  $n_D^{20} = 1.5468$ ); density  $d_4^{20} = 0.650$  (literature value  $d_4^{20} = 0.9060$ ) [9].

- methacrylic acid purchased from Aldrich;  $d_4^{20} = 1.015$ .

- glycidyl methacrylate purchased from Aldrich;  $d_4^{20} = 1.042$ ,  $n_D^{20} = 1.449$ .

- maleic anhydride purchased from Ukrorgsintez (Kyiv, Ukraine); melting point 325.8 K, boiling point 475 K.

2,2'-Azobis(2-methylpropionitrile) in the form of 0.2 M solution in toluene (AMP) was purchased from Aldrich and used as the initiator of LFCT and ICF cooligomerization. It was found for the solution  $d_4^{20} = 0.858$ ,  $n_D^{20} = 1.495$ .

The petroleum ether was a fraction with a boiling range of 313–343 K,  $d_4^{20} = 0.650$ .

### 2.2. Analytical Determination

The number-average molecular weight ( $M_n$ ) of the synthesized CIR was determined using cryoscopy in dioxane. The content of carboxy groups was determined using a back titration method [10]. The softening temperature of CIR was determined using ring-and-ball method [11].

### 2.3. Spectral Measurements

Infrared spectra of CIR with carboxy groups were measured using Nicolet IR 200 (Thermo Electron Co., USA) with GoldenGate ATR diamond crystal. Every spectrum was recorded with  $4 \text{ cm}^{-1}$  resolution. Samples were prepared as powders or were dissolved in acetone.

### 2.4. Synthesis Procedure

LFCT or ICF cooligomerization was carried out in metal ampoules by the capacity of 100 ml. The ampoules

were loaded by the corresponding mixture, blown with an inert gas, closed and placed into a thermostat. After finishing the process the ampoules were cooled to the definite temperature and the matter was precipitated using petroleum ether. The precipitated product was dried in vacuum oven at 313 K. The yields relative to the initial reaction mixture ( $X_1$ ) and main resin-formed components (styrene, indene, coumarone, MAA) ( $X_2$ ) were calculated according to the formulae (1) and (2), respectively:

$$X_1 = \frac{m_r}{m_{IRM}} \cdot 100\% \quad (1)$$

$$X_2 = \frac{m_r}{m_{st} + m_{in} + m_{cm} + m_{MAA}} \cdot 100\% \quad (2)$$

where  $m_r$  – weight of the resulted resin, g;  $m_{IRM}$  – weight of the initial reaction mixture, g;  $m_{st}$ ,  $m_{in}$ ,  $m_{cm}$ ,  $m_{MAA}$  – weights of styrene, indene, coumarone and MAA, respectively.

To determine the conversion of styrene, indene, coumarone and other compounds which may be present in the resin structure, the liquid residue was separated by distillation under vacuum. The product composition was determined to calculate the weight of those components which did not pass into CIR. The conversion of unsaturated compounds ( $X_{unsat}$ ) was calculated according to Eq. (3):

$$X_{unsat} = \frac{m_{unsat}^1 - m_{unsat}^2}{m_{unsat}^1} \cdot 100\% \quad (3)$$

where  $m_{unsat}^1$  and  $m_{unsat}^2$  – weights of unsaturated compounds (styrene, indene, etc.) in the initial reaction mixture and distilled off product, respectively, g.

The content of functional groups, molecular weight and softening temperature were determined for the resulted products.

### 2.5. Chromatographic Investigations

The investigations were carried out using Crystal 2000M gas-liquid chromatograph (Yoshkar-Ola, Russia). The column by the length of 3 m was filled with Inerton-super (0.16–0.20 mm fraction) + 10% tricresyl phosphate. The column temperature was 403 K, evaporator temperature 473 K, detector temperature 473 K. Gas flow rate was 40.0 ml/min.

## 3. Results and Discussion

### 3.1. Influence of Different Factors on the Product Characteristics

Both LFCT and ICF contain styrene, coumarone and indene (Table 1). Under certain conditions the mentioned



compounds are capable to polymerize and form coumarone-indene resins. LFCT cooligomerization was carried out at 353 K for 6 h using AMP as the initiator in the amount of 6.85 g/l. The CIR yield was only 4.1 %. Therefore, to increase the yield, we added styrene in the amount of 7.3 g per 45.2 g of the initial fraction. In such a case the yield increased to 5.2 %. If we additionally used other modifiers (maleic anhydride (MA), methacrylic acid (MAA), glycidyl methacrylate (GMA)), the yield considerably increases compared to LFCT without them (Table 2).

So, the introduction of additional modifier to the initial mixture increases the CIR yield by 3.5–4 times. The resulted solid product, except for that obtained in the presence of MAA, is badly soluble in organic solvents. Therefore, further we studied the effect of cooligomerization temperature, time and AMP amount on the CIR characteristics using the mixture consisted of LFCT, styrene and MAA. The obtained results are represented in Figs. 4–6 and Table 3.

One can see from Fig. 4 that the highest yield is observed using AMP in the amount of 3.82 g/l related to the initial LFCT. Further increase in AMP amount does not increase IRC yield; moreover it decreases the yield relative to the main resin-formed compounds. The possible explanation is following: when we added more than 3.82 g/l AMP, not only the initiated cooligomerization of unsaturated compounds contained in LFCT, styrene and MAA occurs, but also the reaction leading to the recombination of the radicals formed due to AMP decomposition takes place as well (Scheme 1).

The increase in AMP amount favours the proceeding of above-mentioned reaction. Removal of free radicals from the reaction mixture leads to the decrease in CIR yield, the formation of which takes place only *via* initiated cooligomerization. The shape of *curve 2*, Fig. 4 also indicates the absence of unsaturated compounds cooligomerization.

Table 2

#### LFCT cooligomerization in the presence of different modifiers

Mixture composition				Yield relative to the initial mixture		
LFCT		Styrene		Modifier and its amount, mass parts	g	%
ml	mass parts	ml	mass parts			
50	45.2	8	7.3	MA, 2.00	10.3	18.9
50	45.2	8	7.3	MAA, 2.03	10.1	18.5
50	45.2	8	7.3	GMA, 2.15	12.2	22.3

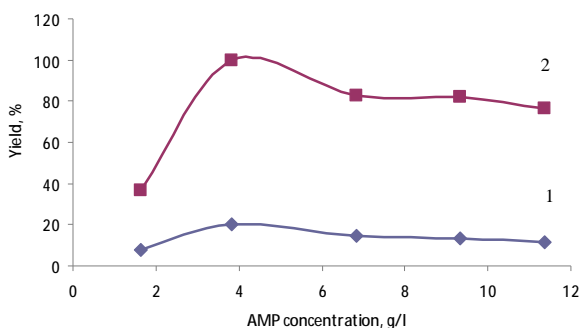
Notes: cooligomerization temperature 353 K, time 6 h, AMP amount 0.5 g.

Table 3

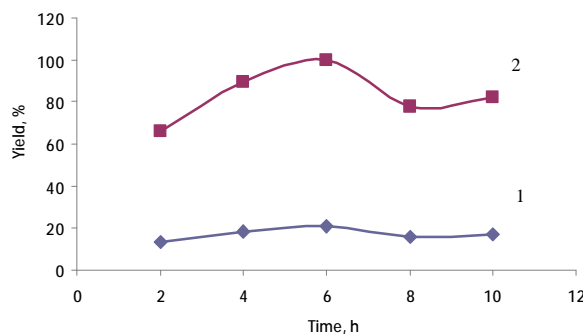
#### Effect of cooligomerization temperature, time and initiator amount on CIR characteristics

Synthesis conditions			CIR characteristics			
T, K	t, h	AMP amount, g/l	CIR symbol	Softening temperature, K	Content of COOH- groups, %	M <sub>n</sub>
80	6	0.00	Cooligomerization does not occur			
80	6	1.64	CIR-1	375	16.0	–
80	6	3.82	CIR-2	391	13.8	950
80	6	6.85	CIR-3	392	12.9	900
80	6	9.32	CIR-4	386	13.1	–
80	6	11.36	CIR-5	381	12.7	–
80	2	3.82	CIR-6	384	14.9	–
80	4	3.82	CIR-7	393	14.9	–
80	8	3.82	CIR-8	391	14.4	–
80	10	3.82	CIR-9	377	12.2	–
60	6	3.82	negligible yield			
70	6	3.82	CIR-10	391	13.7	–
90	6	3.82	CIR-11	394	14.3	–
80	6	3.82	CIR-12	380	10.5	820

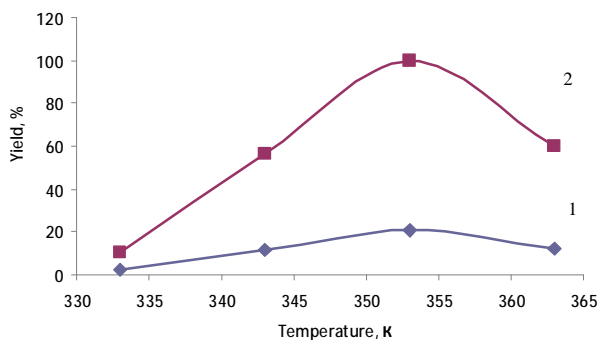
Notes: CIR-1–CIR-11 were synthesized using LFCT; CIR-12 – using ICF. Amounts in the reaction mixture (mass parts): LFCT and ICF – 45.2 and 47.3, respectively; styrene – 7.3; MAA – 2.0.



**Fig. 4.** Effect of AMP concentration on CIR yield relative to the initial mixture (1) and the main resin-formed compounds (2)



**Fig. 5.** Effect of process time on CIR yield relative to the initial mixture (1) and the main resin-formed compounds (2)

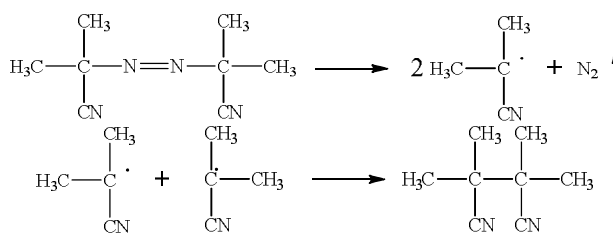


**Fig. 6.** Effect of process temperature on CIR yield relative to the initial mixture (1) and the main resin-formed compounds (2)

When analyzing Fig. 5, one can see that the CIR yield has an extreme value at cooligomerization time of 6 h. The increase in a process time to 10 h decreases the content of carboxy groups in CIR (Table 3). We suggest that apart from cooligomerization reaction, a complex formation with participation of LFCT components takes place. The formation of additional complexes at the initial stage favours the increase in CIR yield. The heating for more than 6 h results in possible destruction of the complexes and further cooligomerization providing the decrease in carboxy groups content due to the entering of styrene, indene and coumarone molecules into the structure (Table 3).

Regarding the temperature effect on CIR yield (Fig. 6) it was determined that CIR is actually not formed at 333 K. At 363 K the CIR yield is decreased (compared with that at 353 K) due to the rapid decomposition of initiator molecules and recombination of formed radicals according to Scheme 1. In addition, at 363 K the cooligomerization reaction with MAA participation is accelerated. The increased content of the carboxyl groups in CIR-11 (Table 3) indicates this fact.

It should be noted that abnormally high resin yield relative to the main resin-formed components is observed, though the conversions of styrene, indene and coumarone are not higher than 30–50 % (see Subsection 3.2). We assume that other initial components also form products



**Scheme 1**

insoluble in petroleum ether, *e.g.* products of naphthalene and its derivatives alkylation, *e.g.* products of naphthalene and its derivatives alkylation, complexes of resins and aromatic compounds, which precipitate together with CIR.

Thus, the optimum conditions for obtaining CIR were determined: cooligomerization temperature 353 K; time 6 h; mixture composition (mass parts) – LFCT (45.2), styrene (7.3), MAA (2.0) and AMP (0.25). The resulted CIR-2 (Table 3) is characterized by the molecular weight of 950 g/mol and carboxy groups content of 13.8 %. CIR-2 yield is 20.0 % relative to the initial mixture and 100.0 % relative to the main resin-formed compounds. The softening temperature is 391 K.

CIR-12 was obtained for the comparison (Table 3). The initial material to synthesize CIR-12 was ICF (Table 1). The resin is characterized by the molecular weight of 820 g/mol and carboxy groups content of 10.5 %. CIR-12 yield is 17.13 % relative to the initial mixture and 62.10 % relative to the main resin-formed compounds. Its softening temperature is 380 K.

To determine the role of LFCT and ICF in the cooligomerization process we carried out polymerization of the mixture without above-mentioned fractions. The investigated mixture consisted of (mass parts) toluene (45.2); styrene (7.3); MAA (2.0) and AMP (0.25). After cooligomerization of such a mixture under optimum



conditions the yield of the resulted product was 8.5 % relative to the initial mixture and 42.6 % relative to the main resin-formed compounds; carboxy groups content was 19.0 %. So, during cooligomerization of styrene and MAA not all monomers participate in cooligomer formation. The results shown in Figs. 4-6 also confirm this fact.

### 3.2. Chromatographic Investigations

The investigations were carried out to establish the participation of the initial mixture components in the process of CIR formation. The procedure described in

Subsection 2.4 was somewhat changed. After cooligomerization the mixture was not precipitated using petroleum ether but vacuumized at 363 K and residual pressure of 2.67 kPa in the presence of inert gas. To determine the content of the individual components the obtained product was analyzed by a gas-liquid chromatography. On the basis of group composition of the initial fractions (Table 1) and conditions for obtaining CIR-2 and CIR-12 the conversions of unsaturated compounds were calculated according to Eq. (3). The results obtained are given in Tables 4 and 5.

Table 4

**Content of the components in the mixtures based on LFCT for obtaining ICR-2**

Component	Component content				Conversion of unsaturated compounds, %
	in the initial mixture		in the distilled off product		
	wt %	g	wt %	g	
Benzene	25.98	15.85	18.95	7.45	–
Toluene	27.86	17.00	36.31	14.27	–
<i>m + p</i> -Xylenes	13.01	7.93	18.55	7.29	–
Styrene	12.85	7.84	11.81	4.64	40.78
Hidrindane	3.24	1.98	3.47	1.36	–
Coumarone	0.96	0.58	1.03	0.40	30.62
Indene	2.92	1.78	2.48	0.98	45.24
Naphthalene	1.32	0.81	0.45	0.18	–
<i>b</i> -Methylnaphthalene	2.22	1.36	absent	absent	–
<i>a</i> -Methylnaphthalene	0.42	0.25	absent	absent	–
Methacrylic acid	3.33	2.03	absent	absent	100.00
Other hydrocarbons	5.48	3.34	6.95	2.73	–
AMP	0.41	0.25	absent	absent	–
Total	100.00	61.00	100.00	39.30	–

Table 5

**Content of the components in the mixtures based on ICF for obtaining ICR-12**

Component	Component content				Conversion of unsaturated compounds, %
	in the initial mixture		in the distilled off product		
	wt %	g	wt %	g	
Benzene	0.95	0.60	1.54	0.57	–
Toluene	17.65	11.13	27.59	10.20	–
<i>m + p</i> -Xylenes	19.29	12.16	24.15	8.94	–
Styrene	13.42	8.46	11.60	4.29	49.24
Hidrindane	9.63	6.07	8.90	3.29	–
Coumarone	2.66	1.68	2.90	1.07	36.09
Indene	8.28	5.22	8.06	2.98	42.90
Naphthalene	3.00	1.89	1.15	0.43	–
<i>b</i> -Methylnaphthalene	6.69	4.22	absent	absent	–
<i>a</i> -Methylnaphthalene	1.24	0.78	absent	absent	–
Methacrylic acid	3.22	2.03	absent	absent	100.00
Other hydrocarbons	13.57	8.56	14.10	5.22	–
AMP	0.40	0.25	absent	absent	–
Total	100.00	63.05	100.00	36.99	–

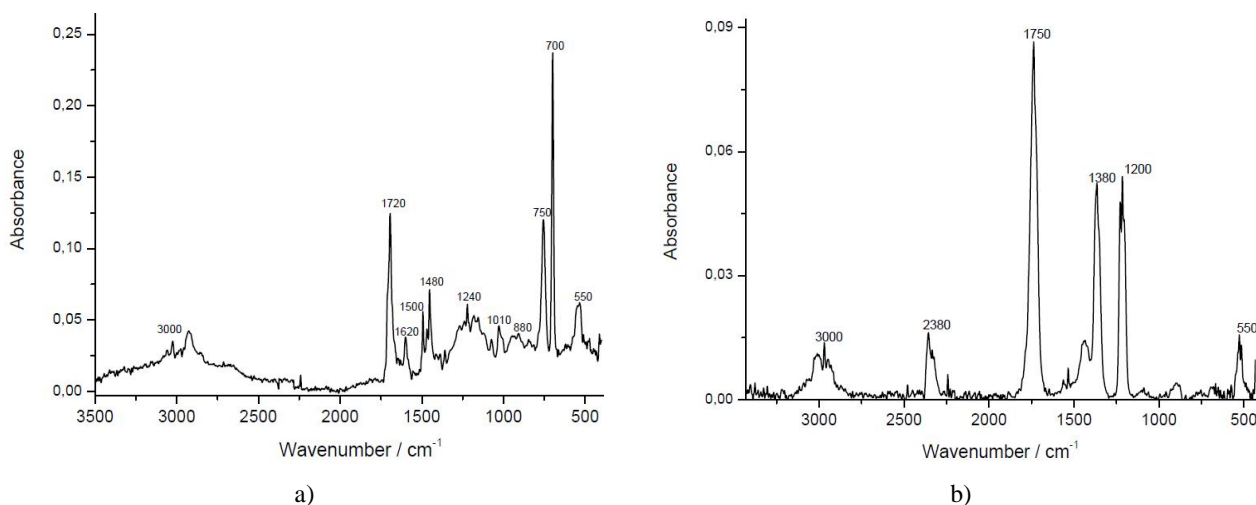


Fig. 7. IR-spectra of CIR-2 (a) and CIR-12 (b)

One can see from Tables 4 and 5 that only MAA totally participates in a polymerization process giving the possibility to obtain ICR with carboxy groups. It is confirmed by the absence of MAA in the distilled off product. In the case of unreacted products distillation the resins yield relative to the initial mixture is 16.72 % for LFCT and 17.13 % for ICF. The obtained results are in agreement with the data represented in Figs. 4-6, especially regarding the abnormal high yield of CIR relative to the main resin-formed components: 83.36 % for LFCT and 62.10 % for ICF. Conversion of unsaturated compounds (%) for LFCT and ICF, respectively: styrene – 40.78 and 49.24; coumarone – 30.62 and 36.09; indene – 45.24 and 42.90. Therefore, the high yield of CIR relative to the main resin-formed compounds (the same as in the case of resin precipitation) is explained by the fact that a part of heavy components and products of aromatics conversion cannot be distilled from the resin at 363 K and residual pressure of 2.67 kPa. For instance, the initial content of *a*- and *b*-naphthalines is sufficiently high (Table 5) but they are absent in the product (except for naphthalene).

### 3.3. IR-Spectroscopic Investigations

IR-spectroscopy was used to confirm the structure of the synthesized CIR and the presence of free carboxy groups in the structure. The presence of free carboxy groups was confirmed earlier by a chemical method and their amount is given in Table 3.

IR-spectra of CIR-2 and CIR-12 are given in Fig. 7. Despite their similarity, the spectra differ by the content of benzene substituted fragments which are confirmed by the absorption bands at 750, 700 and 550 cm<sup>-1</sup>. It indicates

that molecules of styrene, hidrindane and coumarone more actively contribute to the formation of CIR-12 compared with CIR-2. This statement is in agreement with the data given in Tables 4 and 5. The presence of coumarone fragment in CIR-2 and CIR-12 molecules is confirmed by the absorption bands at 1200–1100 cm<sup>-1</sup> related to the ether bond in alicyclic hydrocarbons. The fragments of aromatic compounds characterizing styrene, indene, and coumarone are confirmed by three absorption bands at 1620, 1500 and 1480 cm<sup>-1</sup>. The presence of free carboxy groups in the synthesized products is confirmed by the intensive absorption band at 1750 and 1720 cm<sup>-1</sup> for CIR-12 and CIR-2, respectively, which are typical of stretching vibrations of carbonyl group in the acid. The presence of hydroxy group in the acid is confirmed by absorption band at 3000 and 1010 cm<sup>-1</sup>.

## 4. Conclusions

New coumarone-indene resins (CIR) with carboxy groups were synthesized *via* initiated cooligomerization with the addition of known monomers on the basis of light fraction of coal tar which is produced at JSC "Zaporizhkoks" (Ukraine) and its fraction boiling out within 423–463 K. The best results were obtained with the addition of styrene and methacrylic acid in the presence of 2,2'-azobis(2-methylpropionitrile) in the amount of 3.82 g/l. It was confirmed by the gas-liquid chromatography that only methacrylic acid completely undergoes a polymerization reaction. Styrene conversion does not exceed 50 %, coumarone – 37 %, indene – 46 %. The structure of the synthesized CIR with carboxy groups was confirmed by IR-spectroscopy. The presence of carboxy

group was confirmed by adsorption bands at 1750–1720  $\text{cm}^{-1}$  corresponding to the stretching vibrations of carbonyl group and at 3000  $\text{cm}^{-1}$  corresponding to the stretching vibrations of the hydroxy group in the carboxy one.

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### ОДЕРЖАННЯ ІНДЕН-КУМАРОНОВИХ СМОЛ З ЛЕГКОЇ ФРАКЦІЇ КАМ'ЯНОВУГІЛЬНОЇ СМОЛИ 1. ІНДЕН-КУМАРОНОВІ СМОЛИ З КАРБОКСИЛЬНИМИ ГРУПАМИ

**Анотація.** Коолігомеризацією ненасичених сполук, що містяться в легкій фракції кам'яновугільної смоли (ЛФКВС) та її фракції, що випає за температур 423–463 К (ІКФ) з додаванням промислових мономерів розроблений метод одержання інден-кумаронових смол (ІКС) з карбоксильними групами. Як промислові мономери вивчені стирен, малеїновий ангідрид, гліцидилметакрилат та метакрилова кислота. Як ініціатор реакції використано 2,2'-азо-біс-(2-метилпропіонітрил) у вигляді 0,2М толуольного розчину. Встановлено вплив природи мономерів, кількості ініціатора, температури та тривалості реакції на вихід та характеристику отримуваних ІКС. Структура синтезованих ІКС підтверджена ІЧ-спектроскопічними дослідженнями. Мас-хроматографічними дослідженнями встановлено конверсію ненасичених сполук в процесі одержання ІКС з карбоксильними групами.

**Ключові слова:** легка фракція кам'яновугільної смоли, інден-кумаронова смола, стирен, малеїновий ангідрид, гліцидилметакрилат, метакрилова кислота, 2,2'-азо-біс-(2-метилпропіонітрил), коолігомеризація, ІЧ-спектроскопія, хроматографія.